Searching PAJ Page 1 of 1

# PATENT ABSTRACTS OF JAPAN

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# (54) THERMALLY CONDUCTIVE SHEET FOR SHIELDING ELECTROMAGNETIC WAVE (57) Abstract:

PROBLEM TO BE SOLVED: To obtain a thermally conductive sheet for shielding electromagnetic wave exhibiting excellent machinability, productivity, shape holdability and conductivity.

SOLUTION: A conductive silicone rubber layer filled with pitch based short carbon fibers is applied, on at least one side thereof, with an insulating silicone rubber layer filled with a thermally conductive filler to produce a thermally conductive sheet for shielding electromagnetic wave. It is then applied, internally or on the surface thereof, with a resin fiber sheet material coated with metal.



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#### DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to the thermally conductive electromagnetic wave shielding sheet which makes radiators, such as metal, diffuse the heat from the existing febrile electronic parts, and shields an electromagnetic wave noise.

[0002]

[Description of the Prior Art]The structure which lowers thermal contact resistance is taken by making thermally conductive silicone rubber with thermally conductive silicone grease or pliability intervene between a heater element and a radiator as the thermal diffusion method of a heater element conventionally. If thermally conductive silicone rubber with low hardness is used, the modification and damage accompanying sticking by pressure of a heater element and a radiator can be prevented, and the unevenness at the time of mounting the heater element from which a size and height differ by high density can be absorbed. [0003]On the other hand, many electronic intelligence apparatus is used by progress of communication information art in recent years, and apparatus, reduction of the spurious radiation noise from an element, and protection from an extraneous noise are strongly demanded noting that the emitted electromagnetic waves cause malfunction of electronic equipment. A possibility that the electromagnetic waves generated from a cellular phone, a personal computer, a game machine, etc. will have an adverse effect on a human body is pointed out, and the material and the method of shielding electromagnetic waves are examined. As an electromagnetic wave shield object, the conductive surface treatment thing by composite, plating, vacuum evaporation, paint, etc. which mixed a metaled board, foil, a mesh, the conductive coat, and the conductive bulking agent is used. [0004]

[Problem(s) to be Solved by the Invention]Since these electromagnetic wave shield objects

have the dramatically hard surface and adhesion is bad, another parts as a radiating material are needed. Metaled boards had become a cause by which specific gravity barred the weight saving of electronic equipment highly, a conductive coat and conductive surface treatment required cost, and the badness of productivity had become a problem.

[0005]Conventionally, the thermally conductive sheet which composite-ized the conductive material is proposed. To JP,6-291226,A, for example, the layered product of a metallic foil and the heat dissipation silicone sheet of specific hardness, The cooling structure of the semiconductor device using the silicone radiation sheet of the specific hardness which has a metal mesh shape thing etc., and the heat-conducting characteristic sheet provided with the wire gauze which becomes JP,9-55456,A from the metal of high thermal conductivity is described by JP,7-14950,A.

[0006]These thermally conductive sheets aim at high thermal conductivity, it was not developed in quest of electromagnetic wave shielding, and sufficient electromagnetic wave shielding characteristic is not acquired. Since the metallic foil metallurgy network was used, there was a problem in productivity, such as damaging in the case of decision or bending work.

[0007]In JP,5-17720,B, the heat dissipation shield sheet which produced the conductive polymer by screen-stencil and laminated the electrical insulation layer to both sides is proposed. This sheet can avoid the problem of the productivity at the time of decision or bending work by using not a metallic foil metallurgy network but a conductive polymer. However, there was a problem that electromagnetic wave shielding characteristic sufficient since it is limited to the material which can screen-stencil a conductive layer could not be revealed. Since both sides of a conductive layer have an electrical insulation layer, the electric interengagement of a sheet and the zero bolt power line way of apparatus is uncertain, and it is difficult to acquire an electromagnetic wave shielding characteristic certainly.

[Means for Solving the Problem] This invention solves the above-mentioned technical problem, has thermally conductive and electromagnetic wave shielding both, and provides a thermally conductive electromagnetic wave shielding sheet excellent in processability, productivity, shape retentivity, and conductivity.

[0009]At least on namely, one side of a conductive silicone rubber layer filled up with a short-fiber-shape pitch based carbon fiber. It is a thermally conductive electromagnetic wave shielding sheet which has a sheet like object of a resin fiber covered with metal by an inside or the surface of a thermally conductive electromagnetic wave shielding sheet which laminated an insulating silicone rubber layer filled up with a thermally conductive filler. Metallic coating of a sheet like object of a resin fiber is the thermally conductive electromagnetic wave shielding sheet currently made in paints containing an electroless deposition method, physical vapor

deposition, or metal. At least on one side of a conductive silicone rubber layer filled up with a short-fiber-shape pitch based carbon fiber. It is a thermally conductive electromagnetic wave shielding sheet which has a sheet like object which becomes an inside or the surface of a thermally conductive electromagnetic wave shielding sheet which laminated an insulating silicone rubber layer which blended a thermally conductive filler from a mixture of a conductive fiber and a resin fiber.

[0010]A conductive fiber is a thermally conductive electromagnetic wave shielding sheet which is at least one sort chosen from a metal fiber, a resin fiber covered with metal, carbon fiber, and carbon fiber covered with metal. Metal is a thermally conductive electromagnetic wave shielding sheet which is at least one sort chosen from copper, nickel, silver, chromium, gold, tin, iron, and aluminum. Hardness after hardening of an insulating silicone rubber layer filled up with a thermally conductive filler is a thermally conductive electromagnetic wave shielding sheet which is less than 30 by the Aska C hardness.

[0011]

[Embodiment of the Invention]The thermally conductive electromagnetic wave shielding sheet in this invention, Thermal conductivity at least on one side of the conductive silicone rubber layer highly filled up with the existing conductive short-fiber-shape pitch based carbon fiber. As a sheet like object which has electromagnetic wave shielding on the inside or the surface of a thermally conductive electromagnetic wave shielding sheet which laminated the insulating silicone rubber layer which blended the thermally conductive filler, It is the thermally conductive electromagnetic wave shielding sheet which gave electromagnetic wave shielding and shape retentivity by providing the sheet like object which consists of a sheet like object of the resin fiber covered with metal, or a mixture of a conductive fiber and a resin fiber. In order to prevent the modification and damage accompanying sticking by pressure of a heater element and a radiator, to enlarge a touch area and to lower thermal contact resistance, the hardness after hardening of the insulating silicone rubber layer filled up with the thermally conductive filler is a thermally conductive electromagnetic wave shielding sheet which is less than 30 by the Aska C hardness. The Aska C hardness is the hardness which used and measured the springloaded hardness tester Aska C type based on SRIS 0101 (Society of Rubber Industry, Japan standard) and JIS S6050.

[0012]Hereafter, this invention is explained in more detail. It is preferred to use the optical anisotropy pitch which are high intensity and a rate of high elasticity while being distinguished by a petroleum system or not only a Carboniferous system but an optical anisotropy pitch and the optical-isotropy pitch, and was excellent in chemical resistance and high-temperature-oxidation-proof nature as a pitch based carbon fiber used by this invention. Since it has thermal conductivity with a graphitization pitch high in the direction of fiber length which heat-treated at about 1500-3000 \*\* by using an optical anisotropy pitch as a raw material, it is

desirable. However, even if it performs it after making it into short fiber shape, even if it performs heat treatment for textiles before using short fiber shape, it is not cared about. [0013]In order to raise wettability with silicone rubber, surface treatments, such as electrolytic oxidation, UV refining, corona refining, and coupling agent spreading, may be performed to a pitch based carbon fiber. Although it does not limit especially as fiber length of a staple fiber, it is easy to fill up matrix resin with the range of 20 micrometers - 1 mm of average length, and it is preferred. Since bulk specific gravity will become small, the restoration to matrix resin will become difficult and workability will fall if average length is shorter than 20 micrometers, it is not suitable. Since it twines, and it will be, and textiles cannot be high-filled up but they will produce unevenness on the thermally conductive sheet surface after hardening if average length exceeds 1 mm, it is not suitable.

[0014]As matrix resin in this invention, although silicone rubber, an epoxy resin, urethane resin, fluorocarbon rubber, etc. are mentioned, it excels in processability, heat resistance is high, and small silicone rubber of the temperature dependence of a property value is preferred. It can be considered as a silicone rubber layer with low hardness by furthermore using silicon gel. Such silicone rubber and silicon gel are obtained by hardening publicly known polyorganosiloxane.

[0015]About a curing method, it does not limit and the radical reaction by organic peroxide, the addition reaction which consists of ORGANO hydrogen which has the hydrogen atom combined with the polyorganosiloxane containing a vinyl group and a silicon atom, and a platinum system catalyst, a condensation reaction, etc. are mentioned. Also in it, since it excels in a moldability, pliability, etc. when liquefied addition reaction type polyorganosiloxane is used, it is desirable. Reinforcement nature silica, fire retardant, colorant, a heat-resistant improver, a bonding assistant, a binder, a plasticizer, oil, a concrete retarder, etc. may be added.

[0016]Although the forming process of the thermally conductive sheet in this invention is not limited, press forming, injection molding, extrusion molding, calender molding, roll forming, doctor blade shaping, printing, etc. are mentioned.

[0017]The aluminum oxide which is excellent in thermal conductivity with a thermally conductive filler in this invention, Magnesium oxide, boron nitride, alumimium nitride, aluminium hydroxide, Metallic oxides, such as silicon carbide and a ferrite, metal nitride, metallic carbide, The bulking agent of at least a kind of globular shape, powder state, fibrous, a needle, the shape of a scale, and a pellet type chosen from metal and alloys, such as metal hydroxide, silver, gold, copper, aluminum, magnesium, and a diamond, or graphite is mentioned. At least a kind of thermally conductive filler chosen from the aluminum oxide, magnesium oxide, the boron nitride, alumimium nitride, the silicon carbide, and aluminium hydroxide which are excellent in electric insulation also in it is preferred.

[0018] By furthermore carrying out the surface treatment of the surface of a thermally conductive filler in a publicly known coupling agent etc., it is possible to improve dispersibility. As loadings of a thermally conductive filler, although it changes also with kinds of a thermally conductive filler and polyorganosiloxane, 50 - 95wt% is preferred. When less than 50wt%, thermal conductivity is low, and since the restoration nature to polyorganosiloxane will be inferior, viscosity will rise and processability will get worse if more than 95wt%, it is unsuitable. As a sheet like object which has electromagnetic wave shielding [ which is used in this invention], the sheet like object of the resin fiber covered with metal can be used. [0019]As a sheet like object which has electromagnetic wave shielding [ which is furthermore used in this invention ], the sheet like object which consists of a mixture of a conductive fiber and a resin fiber can be used. A metal fiber, the resin fiber covered with metal, carbon fiber, the carbon fiber covered with metal, and the glass fiber covered with metal are mentioned to a conductive fiber. It can manufacture by the usual technique of becoming a sheet like object which is supple rather than a conductive fiber simple substance, and processing the mixture of a conductive fiber and a resin fiber into a sheet shaped by using the sheet like object which consists of a mixture of a conductive fiber and a resin fiber. For example, it can obtain also with the paper making method indicated to JP,6-55467,B.

[0020]Especially about the construction material of a resin fiber, do not limit and, for example Polyethylene terephthalate (PET) textiles, Polyester fiber, a polyamide fiber, aromatic polyamide textiles, an aramid fiber, The usual textiles, such as a polyimide fiber, acrylic fibers, olefin system textiles, vinyl system textiles, a phenol fiber, fluorine-containing textiles, polyphenylene sulfide textiles, a polyurethane fiber, polybenzimidazole textiles, and cotton, can be used. As a metal fiber, a stainless steel fiber, stainless-steel textiles, a nickel fiber, copper textiles, aluminum textiles, chromium textiles, brass textiles, bronze textiles, etc. are mentioned.

[0021]The resin fiber which constitutes the sheet like object which has electromagnetic wave shielding [ which is used in this invention ], Although the metal covered by carbon fiber and glass fiber is not specified, it is preferred that it is at least one sort chosen from electromagnetic wave shielding good copper, nickel, silver, chromium, gold, tin, iron, and aluminum. The alloy which consists of these metal can be used. Although the method of covering is not limited and covering by physical vapor deposition, such as an electroless deposition method, an electrolytic plating method, a vacuum deposition method, and sputtering process, or the paint containing metal is mentioned, an electroless deposition method can be covered uniformly and is a comparatively cheap method. It may cover with two or more sorts of metal, and an enveloping layer may turn into two or more layers. Even if it performs it after making it into a sheet shaped, even if it performs metallic coating processing before processing it into a sheet shaped, it is not cared about.

[0022]As for the shape of the sheet like object which consists of a sheet like object of the resin fiber of this invention, or a mixture of a conductive fiber and a resin fiber, textile fabrics, a nonwoven fabric, a mesh shape thing, a mesh state thing, a paper-making-like thing, a film, etc. are mentioned. If the thing with a comparatively large ratio of valve opening of textile fabrics, a nonwoven fabric, a mesh shape thing, and a mesh state thing is used especially, silicone rubber will enter into the opening part and reinforcement nature will improve. In order to improve wettability with silicone rubber, surface treatments, such as electrolytic oxidation, UV refining, corona refining, coupling agent spreading, and primer coating, may be performed to the sheet like object of a resin fiber.

[0023]The following examples explain concretely the thermally conductive electromagnetic wave shielding sheet of this invention. The obtained thermal conductivity of each example and comparative example of a thermally conductive sheet was measured with the quick thermal conductivity meter (Kyoto Electronics Manufacturing Co., Ltd. make QTM-500). The electromagnetic wave shielding effect was measured by the ADVANTEST method, and asked for the maximum, the average value, and standard deviation after 5 times measurement. The result of measurement is shown in Table 1 with specific gravity. Shape imitation nature has arranged the thermally conductive electromagnetic wave shielding sheet obtained in the upper part of the substrate which mounted the semiconductor device from which height differs, and made the radiator contact, and what is inferior in O and imitation nature in what has good shape imitation nature was shown as x. The result was summarized in Table 1. [0024]

[Example 1] The sectional view of the composition of the thermally conductive electromagnetic wave shielding sheet of Example 1 of this invention is shown in drawing 1. the short-fibershape pitch based carbon fiber (product made from PETOKA, Inc. mel BUROMMIRUDO) 1 --60wt% -- liquefied filled addition reaction type silicone rubber (made by GE Toshiba Silicones Co., Ltd.), Carry out sheeting with doctor blade shaping, and it is considered as the conductive silicone rubber layer 4, . It is a sheet like object of the resin fiber covered with metal as a sheet like object which has electromagnetic wave shielding on the one side. The PET-fiber nonwoven fabric (Sui-80-301 by SEIREN CO., LTD.) 3 by which Cu-nickel covering was carried out is laminated, further -- the nonwoven fabric side -- as a thermally conductive filler -an aluminum oxide (Showa Denko K.K. make spherical alumina AS-20) -- 80wt% -- the blended liquefied addition reaction type silicon gel (made by GE Toshiba Silicones Co., Ltd.) 2, After carrying out sheeting with doctor blade shaping and considering it as the insulating silicone rubber layer 5, heat cure was carried out and the 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained. What laminated the conductive silicone rubber layer 4 to both sides of the sheet like object 3 which has electromagnetic wave shielding is shown in drawing 2.

## [0025]

[Example 2] It is made to be the same as that of Example 1 except having used the PET-fiber mesh shape thing (Sui-10-26 by SEIREN CO., LTD.) 3 which is a sheet like object of the resin fiber covered with metal and by which Cu-nickel covering was carried out as a sheet like object which has electromagnetic wave shielding, The 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained.

[0026]

[Example 3] The sectional view of the composition of the thermally conductive electromagnetic wave shielding sheet of Example 3 of this invention is shown in <u>drawing 4</u>. After laminating the insulating silicone rubber layer 5 which blended the thermally conductive filler 2 with the conductive silicone rubber layer 4 side of the thermally conductive electromagnetic wave shielding sheet obtained in Example 1, heat cure was carried out and the 1.3-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained.

[0027]

[Example 4] The sectional view of the composition of the thermally conductive electromagnetic wave shielding sheet of Example 4 of this invention is shown in <a href="mailto:drawing-3">drawing 3</a>. the short-fiber-shape pitch based carbon fiber (product made from PETOKA, Inc. mel BUROMMIRUDO) 1 --60wt% -- liquefied filled addition reaction type silicone rubber (made by GE Toshiba Silicones Co., Ltd.), As a sheet like object which carries out sheeting with doctor blade shaping, considers it as the conductive silicone rubber layer 4, and has electromagnetic wave shielding on one side [further], The sheet like object (OTEKKU EMS by Mishima Paper Co., Ltd.) 3 by which paper making was carried out as a conductive fiber using a mixture with an aramid fiber as stainless-steel textiles and a resin fiber is laminated, further -- the conductive silicone rubber layer 4 side -- as the thermally conductive filler 2 -- an aluminum oxide (Showa Denko K.K. make spherical alumina AS-20) -- 80wt% -- the liquefied addition reaction type silicon gel (made by GE Toshiba Silicones Co., Ltd.) with which it was filled up, After carrying out sheeting with doctor blade shaping and considering it as the insulating silicone rubber layer 5, heat cure was carried out and the 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained.

[0028]

[Example 5] The carbon fiber (BESUFAITO MC by Toho Rayon Co., Ltd.) which plated and covered nickel as a conductive fiber as a sheet like object which has electromagnetic wave shielding, Laminating the sheet like object 3 by which paper making was carried out using a mixture with an aramid fiber as a resin fiber, other composition obtained the 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet like Example 1. [0029]

[Comparative example 1] liquefied addition reaction type silicon gel (made by GE Toshiba

Silicones Co., Ltd.) -- aluminum oxide dust (Showa Denko K.K. make spherical alumina AS-20) -- 80wt% -- the silicone compound with which it was filled up, Sheeting was carried out with doctor blade shaping, heat cure was carried out and hardness obtained the 1.0-mm-thick thermally conductive sheet by the Aska C hardness 27.

[0030]

[Comparative example 2] After laminating 15-micrometer-thick aluminum foil on one side of a silicone compound used by the comparative example 1, heat cure was carried out, and the 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained. [0031]

[Comparative example 3] To both sides of the PET-fiber nonwoven fabric (Sui-80-301 by SEIREN CO., LTD.) which is a sheet like object of the resin fiber covered with metal and by which Cu-nickel covering was carried out. After laminating the silicone compound used by the comparative example 1 with doctor blade shaping, heat cure was carried out, and the 1.0-mm-thick thermally conductive electromagnetic wave shielding sheet was obtained. [0032]

# [Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	比較例 1	比較例 2	比較例 3	
熱伝導率		W(m⋅K)	2. 8	2. B	1. 8	2. 7	2. 7	1. 0	1. 3	1. 0
電磁波シ -ルド 効 果	最大值	dВ	44. 2	5 3. 4	49. 5	35. 4	50, 1	0. 6	54. 2	43. 2
	平均值(;=5)	dB	42.6	50. 9	<b>4</b> 0. 6	3 2. B	48. 2	0. 3	51. 5	34. 4
(電界 500Mz )	標準偏差		1. 11	1.58	3. 14	2. 24	1. 26	0. 22	3. 13	8. 50
比 重			1. 8	1. 8	2. 1	1. 9	1. 9	2. 3	2. 4	2. 3
形状追随性			0	0	0	0	0	0	×	0

[0033]As shown in Table 1, although the comparative example 1 is excellent in shape imitation nature, its thermal conductivity is low, and most electromagnetic wave shielding effects do not have it. Although an electromagnetic wave shielding effect is large, the comparative example 2 cannot have the bad shape imitation nature of aluminum foil, cannot be bad, and cannot absorb unevenness of the heater element from which a size and height differ. [ of workability, such as bending work and decision processing, ]

[0034]Although it is large, since the conductive layer is very thin, the maximum of an electromagnetic wave shielding effect has the uncertain electric interengagement of a sheet and the zero bolt power line way of apparatus, and it is difficult for the comparative example 3 for variation to arise in a value and to acquire an electromagnetic wave shielding characteristic certainly. The specific gravity of the thermally conductive sheet obtained since the specific gravity of the thermally conductive filler to add was large will also become large, and the comparative examples 1-3 will be a factor which bars the weight saving of electronic equipment.

## [0035]

[Effect of the Invention]The conductive silicone rubber layer with which the thermally conductive electromagnetic wave shielding sheet of this invention filled up the short-fiber-shape pitch based carbon fiber, By laminating the insulating silicone rubber layer filled up with the thermally conductive filler, and having a sheet like object which consists of a sheet like object of the resin fiber covered with metal by an inside or the surface, or a mixture of a conductive fiber and a resin fiber, It has [ high thermal conductivity and electromagnetic wave shielding ], and since flexible silicone rubber is used, it excels in shape imitation nature. [0036]The specific gravity of the thermally conductive sheet obtained since the specific gravity of a pitch based carbon fiber was small is also small. The sheet like object which consists of a sheet like object of a resin fiber and a mixture of a conductive fiber and a resin fiber also plays a reinforcing member's role, and becomes the thing excellent in workability and shape retentivity. It becomes possible for it to be stabilized in laminating the conductive silicone rubber layer filled up with the short-fiber-shape pitch based carbon fiber, and to make a metal radiator and a case contact electrically, and the reliability of an electromagnetic wave shielding effect can be improved.

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#### CLAIMS

## [Claim(s)]

[Claim 1]At least on one side of a conductive silicone rubber layer filled up with a short-fiber-shape pitch based carbon fiber. A thermally conductive electromagnetic wave shielding sheet which has a sheet like object of a resin fiber covered with metal by an inside or the surface of a thermally conductive electromagnetic wave shielding sheet which laminated an insulating silicone rubber layer which blended a thermally conductive filler.

[Claim 2] The thermally conductive electromagnetic wave shielding sheet according to claim 1 currently made in paints in which metallic coating of a sheet like object of a resin fiber contained an electroless deposition method, physical vapor deposition, or metal.

[Claim 3]At least on one side of a conductive silicone rubber layer filled up with a short-fiber-shape pitch based carbon fiber. A thermally conductive electromagnetic wave shielding sheet which has a sheet like object which becomes an inside or the surface of a thermally conductive electromagnetic wave shielding sheet which laminated an insulating silicone rubber layer which blended a thermally conductive filler from a mixture of a conductive fiber and a resin fiber.

[Claim 4]The thermally conductive electromagnetic wave shielding sheet according to claim 3 which is at least one sort as which a conductive fiber is chosen from a metal fiber, a resin fiber covered with metal, carbon fiber, and carbon fiber covered with metal.

[Claim 5] The thermally conductive electromagnetic wave shielding sheet according to any one of claims 1 to 4 whose metal is at least one sort chosen from copper, nickel, silver, chromium, gold, tin, iron, and aluminum.

[Claim 6] The thermally conductive electromagnetic wave shielding sheet according to any one of claims 1 to 5 whose hardness after hardening of an insulating silicone rubber layer which blended a thermally conductive filler is less than 30 by the Aska C hardness.

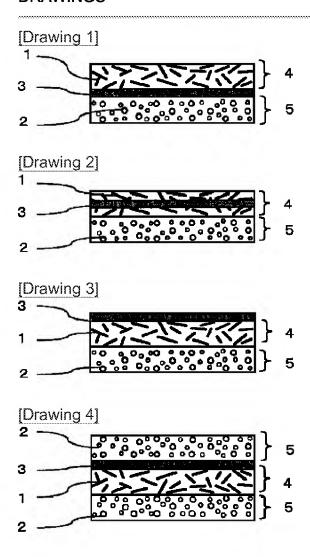
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### **DRAWINGS**



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